

SUBSTRATE UTILIZATION APPROACH FOR DESIGN OF NITROGEN CONTROL

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ABSTRACT: A combined nitrification/denitrification (N/D) system was investigated as a method for reducing the waste load of tannery waste to proposed EPA levels. Present design criteria for nitrate reduction are inadequate not only for the system under study but for a spectrum of interesting process variations. A biokinetic approach to deal with this shortcoming was developed. The anoxic zone of the combined N/D system is viewed as a plug flow reactor with internal recycle; and substrate utilization kinetics of this reactor are examined by use of a batch biokinetic device. Oxygen and nitrate utilization were found to be stoichiometrically related and a function of the ratio of incoming COD (chemical oxygen demand) to sludge mass. Using the method developed, oxygen utilization was found to be an excellent measure of nitrate reduction kinetics.

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INTRODUCTION

Combined nitrification/denitrification (N/D) is best described by considering the integrated nitrification and denitrification functions as separate unit operations. In Fig. 1, biological nitrification is shown as occurring in the first of two successive activated sludge treatment systems, with biological denitrification occurring in the second. Generally, nitrification is accomplished either in a constant stirred ("complete mixed") reactor basin, or in an oxidation ditch under operating conditions of high oxygen tension (greater than 2 mg/L of oxygen) and low sludge wasting (less than 10% of inventory wasted per day) (11,12). The imposed long sludge residence time and typically long hydraulic detention time (often 10 hr or more), results in a basin-mixed liquor that is relatively homogeneous, with a non-sludge fraction that is virtually identical to that of the clarified effluent. The basin mixed liquor is therefore high in nitrate and low in soluble total Kjeldahl nitrogen (TKN), biochemical oxygen demand (BOD), and chemical oxygen demand (COD).

The nitrate can be removed from this effluent in a non-aerated activated sludge treatment system (denitrification). Here, the incoming COD is metabolized with nitrate (rather than oxygen) serving as the oxidant. In the process, the nitrate is reduced to nitrogen gas. Except for the exclusion of oxygen, operating conditions are similar to those of a conventional activated sludge treatment system.

The earliest combined nitrification/denitrification work of note was that of Ludzack and Ettinger (7). The laboratory system they studied is shown in Fig. 2. The system is an anoxic zone followed by an aerobic zone. Influent waste is fed to the anoxic zone where it is oxidized by nitrate produced in, and recycled from, the aerobic zone operated under extended aeration conditions. Results for the most part were qualitative;

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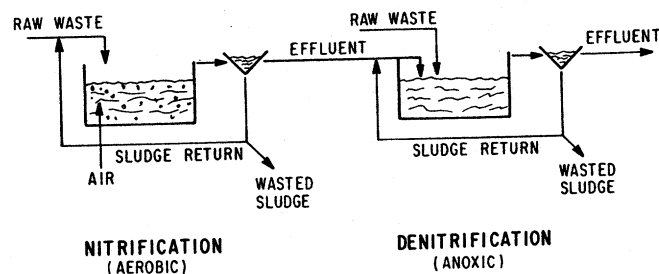


FIG. 1.—Biological Nitrification and Denitrification

however, among the conclusions drawn were that: (1) Conversion of wastewater nitrogen to nitrate with associated denitrification was feasible; (2) processes involving associated nitrification and denitrification have the potential of providing superior effluent (from a nitrogen standpoint) at lower air requirements; and (3) dilute wastes decrease process advantages. Rate information was not obtained.

Wuhrmann (14) reversed the treatment sequence, eliminating the need for mixed-liquor recycling. In this case, the nitrate is reduced to nitrogen gas through the endogenous respiration of the sludge as supported by sludge burn down.

In 1973, Barnard (3) brought both these concepts together in treating a municipal wastewater and demonstrated several important factors (Fig. 3). In his system, Barnard used a two-stage recycle system as per Ludzack and Ettinger, followed by a single-stage anoxic endogenous zone as per Wuhrmann, and lastly by a short aerobic stage added to prevent sludge bulking in the clarifier. Barnard investigated several mixed-liquor recycle ratios (defined as the rate of recycle flow divided by the feed rate) and ultimately suggested a ratio of 4:1. Sludge recycle ratio was 1:1. Barnard demonstrated that the rate of nitrate reduction achieved in the second anoxic basin (i.e., the endogenous respiration rate) is substantially lower than the rate achieved in the first basin. It was thus made clear that nitrate reduction rate is influenced by the influent waste.

Drawing on Barnard's findings, it becomes clear that with a high TKN wastewater: (1) The four-basin approach is of questionable value due to the excessively large basin required for low rate, endogenous respira-

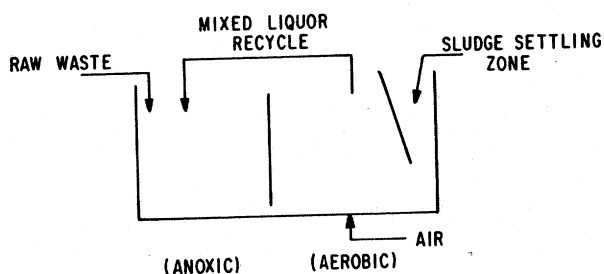


FIG. 2.—Combined Nitrification/Denitrification Process of Ludzack and Ettinger

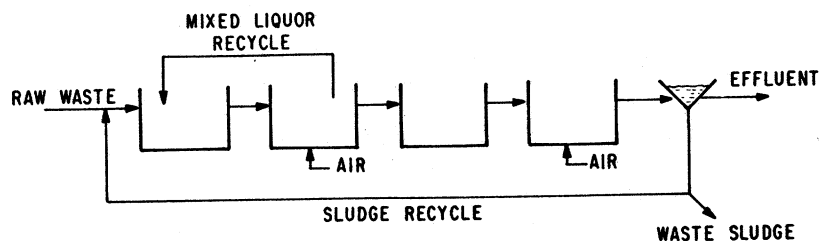


FIG. 3.—The Bardenpho Nitrification/Denitrification Process

tion; and (2) the first anoxic basin should be designed to take advantage of the influent waste concentration. The configuration we have been studying is shown in Fig. 4. The system is essentially a return to the principle proposed by Ludzack and Ettinger, but with the addition of a staged front end. Using this design we have been able to reduce a 200 mg/L TKN wastewater to about 15 mg/L TKN and 5 mg/L ammonia (at a recycle ratio of 15:1), while at the same time attaining a nitrate removal rate of consistently over 0.1 mg/mg day (10).

Although this process represents a substantial improvement in nitrate removal, it is not immediately clear from the above results what the kinetics are and how to incorporate them into a rational design. In addition, an issue that exacerbates the design problem is that the high recycle, makes direct comparison to more conventionally operated systems quite difficult.

Approach.—Our approach has been to determine the kinetics of nitrate reduction, by developing a relationship between nitrate utilization and oxygen utilization, and then study the more tractable problem of oxygen utilization. This view of the kinetics provides two distinct benefits. First, analytical difficulties of measuring small changes (differences) in nitrate concentration, COD concentration, and volatile suspended solids (VSS) content have been eliminated and replaced with the analysis of average VSS, and initial food-to-mass ratio and oxygen uptake rate. Second, we have made it possible to develop nitrate reduction kinetics from oxygen uptake information close at hand. Thus for an extended aeration facility considering modification to include nitrate reduction, the information required may be obtained from studies of their present aeration basin.

Reactor Scheme.—The reactor scheme is shown in Fig. 5. The mathematics are similar to that presented by Argaman and Miller (2). The anoxic zone is viewed as a plug flow type reactor in which the feed

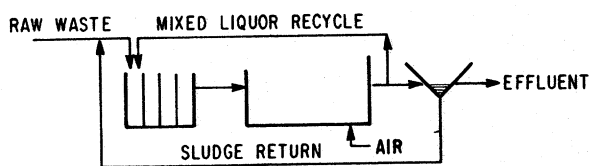


FIG. 4.—Combined Nitrification/Denitrification

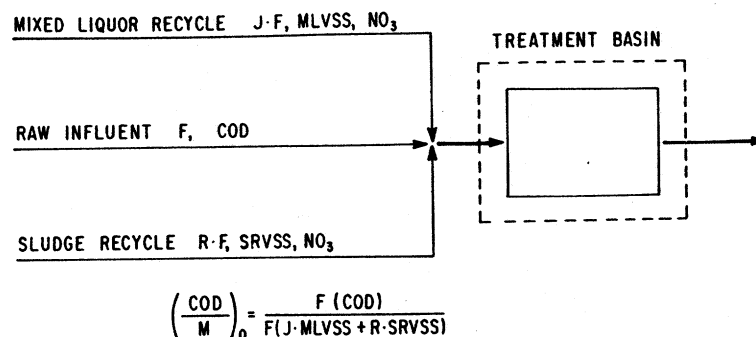


FIG. 5.—Anoxic Zone Reaction Model

stream is a composite of three individual smaller streams. In the center, raw influent flows at rate F (L/hr) and contributes essentially all the removable COD. The waste loading rate is F times the COD concentration (mg/L). Note that either a total or soluble COD basis may be used. At the top, the mixed-liquor recycle stream flows at a rate J times F and contributes nitrate at a rate of JF times the nitrate concentration (mg/L) and sludge mass at a rate of JF times the mixed liquor volatile suspended solids (MLVSS, mg/L). The sludge recycle contributions are calculated in a similar manner. The initial COD-to-mass ratio $(\text{COD}/M)_0$ can be calculated as shown.

$$\left(\frac{\text{COD}}{M}\right)_0 = \frac{F(\text{COD})}{F(J \cdot \text{MLVSS} + R \cdot \text{SRVSS})} \dots\dots\dots (1)$$

in which SRVSS = the sludge recycle volatile suspended solids (mg/L).

This is the ratio of the influent COD mass flow rate to the VSS mass flow rate, rather than the standard definition of food-to-mass ratio. The COD in both the mixed-liquor recycle and sludge recycle is ignored, on the assumption that with industrial strength wastes undergoing extended aeration treatment, the biodegradable contribution from these sources is a minor fraction of the COD entering the system. Lastly, it must be recognized that when our attention is focused within the zone marked by a dashed line (Fig. 5), the hydraulic residence time is markedly different from the detention time. That is, if a total of six times the feed rate flows into the reactor, a residence time of 1 hr within the zone is equivalent to a 6-hr detention time based on feed rate. The reason for stressing this point will be made clear in the discussion of results.

Kinetics.—In a conventional extended aeration system, where only a minor fraction of the COD is transformed into biomass, it is reasonable to take as given that, the rate at which the chemical oxygen demand is consumed is proportional to the rate of use of the oxidant required to consume it.

$$\frac{-d \text{COD}}{dt} = \left(\frac{1}{Y_1}\right) \left(\frac{-d \text{O}_2}{dt}\right) = \left(\frac{1}{Y_2}\right) \left(\frac{-d \text{NO}_3}{dt}\right) \dots\dots\dots (2)$$

in which Y_1 and Y_2 are yield coefficients dependent on the stoichiometry.

Second, the rate of consumption of each of these substrates (i.e., nitrite, oxygen, and COD) can be accurately described as the sum of a maintenance constant, B (mg substrate/mg sludge/hr), plus an accelerated rate term which is a function of COD ($f(\text{COD})$).

$$\text{Substrate utilization rate} = f(\text{COD}) + B \cdot M \quad (\text{mg substrate/hr}) \dots\dots (3)$$

in which M = the sludge mass.

Third and last, we take as given, results of our earlier work (9) that the accelerated rate terms are approximately first order with respect to COD concentration and that the yield factor relating oxygen use to nitrate use is 40%–50% of that predicted on an electron equivalent basis (9).

$$-\left(\frac{d \text{COD}}{dt}\right)_{\text{acc}} = K \cdot \text{COD} \dots\dots\dots (4)$$

During the initial reaction period, this accelerated rate is typically quite large in comparison to the maintenance level of substrate usage. For this reason it should be possible to integrate the accelerated rate term as an independent entity, without creating significant numerical error. Granting this assumption, the first order COD equation (Eq. 4) can be solved for COD in terms of an initial COD content (COD_0) and an exponential decay with time (Eq. 5).

$$\text{COD} = \text{COD}_0 e^{-Kt} \dots\dots\dots (5)$$

In turn, this expression can be substituted into Eq. 4 yielding:

$$-\left(\frac{d \text{COD}}{dt}\right)_{\text{acc}} = K \text{COD}_0 e^{-Kt} \dots\dots\dots (6)$$

Using the appropriate constant to convert COD to oxygen, this expression can be used as the accelerated rate term in an oxygen utilization rate (OUR) equation of the form shown on Eq. 3; dividing through by the sludge mass (M mg of VSS), places this equation on a per unit mass of sludge as shown.

$$\frac{d\left(\frac{\text{O}_2}{M}\right)}{dt} = A \left(\frac{\text{COD}_0}{M}\right) e^{-Kt} + B' \quad (\text{mg O}_2/\text{mg sludge} \cdot \text{hr}) \dots\dots\dots (7)$$

in which $B' = BY_1$ and $A = KY_1$. Note that the result is a specific oxygen uptake rate equation which is a function of an initial COD to mass ratio (COD_0/M), a function of time which is the residence time in the treatment basin, and a function of the maintenance level oxygen uptake rate.

Experimentally, this is the relationship sought. Once obtained, it can be integrated

$$\Delta\left(\frac{\text{O}_2}{M}\right) = \left(\frac{A}{K}\right)(1 - e^{-Kt}) + B't \dots\dots\dots (8)$$

and by incorporating the appropriate oxygen to nitrate conversion factor, converted to a nitrate use prediction equation.

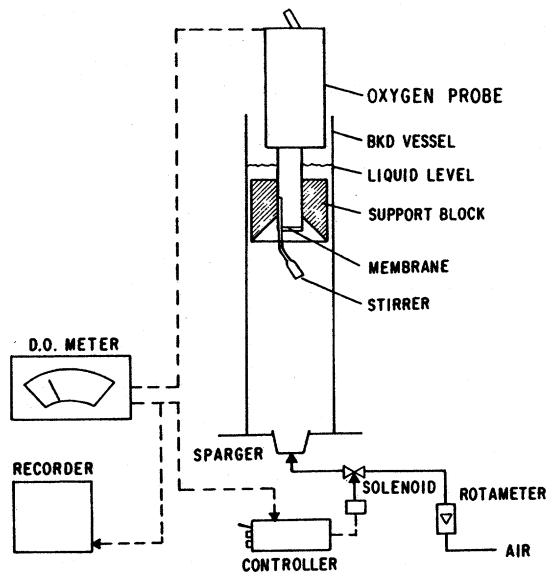


FIG. 6.—Biokinetic Device

$$\Delta\left(\frac{\text{NO}_3}{M}\right) = A'\left(\frac{\text{COD}}{M}\right)_o (1 - e^{-Kt}) + B''t \quad \text{mg NO}_3/\text{mg sludge} \dots\dots\dots (9)$$

in which $A' = Y_2$; $B'' = Y_2/Y_1 B'$; and $(\text{COD}_o/M) = (\text{COD}/M)_o$.

Experimental.—The apparatus we used was described by Jacobson in 1978 (4) in his research on biological reclamation of feed lot waste (Fig. 6). Interestingly, he operated this apparatus at high COD-to-mass ratio in order to measure sludge growth while maintaining relatively constant

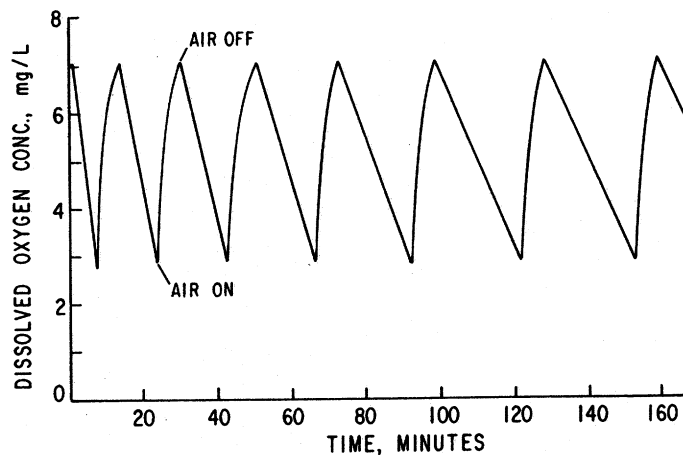


FIG. 7.—Typical Oxygen Uptake Rate Data

substrate concentration. Here, work is at the opposite extreme in order to measure substrate utilization at constant biomass.

The heart of the apparatus is a cylindrical Plexiglas vessel approximately 300 ml in volume—the volume of the standard BOD bottle. (Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.) At the bottom is an airstone and at the top a support block to hold a Yellow Springs Instruments oxygen probe.

In operation, mixed liquor in the vessel is initially aerated to about 7.5 mg/L O_2 , and the air is then automatically turned off (Fig. 7). Oxygen depletion (i.e., oxygen uptake) is then measured on a Yellow Springs dissolved oxygen monitor (model 54) and recorded on a Perkin-Elmer (model 56) strip chart recorder as outlined by Aiba et al. (1). When the oxygen content drops to about 1.5 mg/L, the controller opens the solenoid valve, and the vessel is aerated once again to 7.5 mg/L O_2 whereupon the solenoid is again shut off. The cycle is then repeated.

Initial COD-to-mass ratios were varied from 0.01–0.06 by charging the vessel with various ratios of influent waste and nitrified mixed liquor from a continuous laboratory scale nitrification/denitrification system operated at a ratio just under 0.04. The continuous system provided approximately 3,000 mg/L MLVSS. Experiments could be repeated by allowing the vessel contents to partially settle, withdrawing a specified volume of clarified mixed liquor, and replacing it with an equal volume of raw waste. The results were found to replicate well as long as the oxygen consumed in each run matched or slightly exceeded the COD applied.

A series of nitrate utilization experiments were also conducted in the 0.01–0.06 initial COD-to-mass range, again using blends of nitrified mixed liquor and raw waste from the continuous treatment system. In these experiments a covered 2 L vessel, continuously sparged with nitrogen, was utilized. After incorporation of the raw waste, samples were withdrawn periodically over a 3-hr period, quickly filtered through glass wool and filter paper, and analyzed for nitrate by the cadmium reduction method (8).

Raw Materials.—Tannery wastewater was used throughout this study. End-of-pipe tannery effluent is a composite of a series of highly complex

TABLE 1.—Chrome Tannery Effluent Stream Contributions*

Effluent stream (1)	Flow, as a percentage (2)	BOD, as a percentage (3)
Soaking	11.8	17.7
Unhairing	11.8	58.9
Liming	23.5	11.8
Bating	14.1	1.0
Chrome tanning	3.5	4.7
Retan, coloring, and fat liquoring	23.5	2.4
Finishing	11.8	3.5
Total	100.0	100.0

*Thorstensen, T. C. (1976).

TABLE 2.—Approximate Composition of Lime-Sulfide Unhairing Effluent

Effluent (1)	Unhairing effluent, in milligrams per liter (2)	Physical-chemical pretreated unhairing effluent, in milligrams per liter (3)
BOD ₅	14,000	2,000
COD	31,600	4,700
Sulfide (as s ⁻)	2,000	<1
TKN (as N)	3,000	420
Ammonia (as N)	200	60
Nitrite (as N)	—	<1
Nitrate (as N)	—	<1
Phosphate (as P)	—	<5
Alkalinity (as CaCO ₃)	18,000	250
pH	12	4

processing effluents (Table 1) (6,13). In our view, the best prospects for effective treatment of the composite effluent lie in: (1) The physical-chemical pretreatment of segregated high-load waste streams followed by, (2) the pooling and biological treatment of the chrome-free streams not suitable for recycle or reuse. We have, therefore, developed a physical-chemical (P/C) pretreatment for limesulfide unhairing effluent—the most concentrated of the effluent streams. This P/C-treated effluent has served as the substrate in biological treatment studies (5). In P/C pretreatment, over 95% of the lime and sulfide and over 80% of the COD and total Kjeldahl nitrogen (TKN) were removed (Table 2). Pretreatment consists of fat skimming; carbonation and precipitation for lime removal; acidification, degasification, and filtration for sulfide and protein removal. In the process, waste is acidified in-line and pumped to a vacuum degasification chamber where hydrogen sulfide is removed and readsorbed in sodium hydroxide. The degasified waste is then pumped to a Shriver press for protein removal. Sludge for all experiments was obtained from our laboratory scale continuous nitrification/denitrification treatment unit. The sludge residence time for the unit was 20 days.

RESULTS

Fig. 8 shows selected results of an experiment performed in triplicate at an initial COD/M of 0.0175. The Y-axis is specific oxygen uptake rate (SOUR) given in mg O₂/hr per mg sludge. A best fit for the SOUR versus time data was established by a nonlinear regression technique which determines minimum error square. The resulting equation is shown as a solid line. An *F* test indicated that this equation satisfactorily represented the data at the 95% confidence level.

Fig. 8 shows a key design factor. Note that although this represents batch data, one can view increasing time on the time axis in terms of marching down the length of a plug flow treatment basin. Thus, the initial rate of COD oxidation is substantially higher than the maintenance level, but it appears that after a 3/4 hr residence time, the reaction rate has dropped to a constant, COD-independent maintenance level.

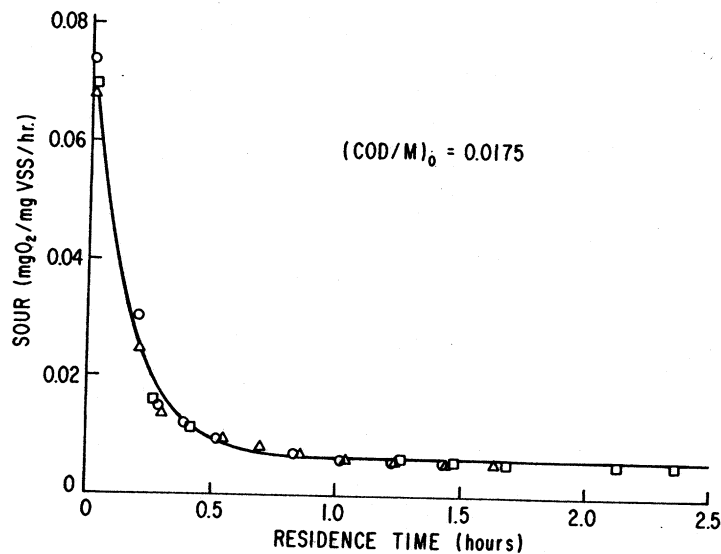


FIG. 8.—Specific Oxygen Uptake Rate as a Function of Time, Regression Curve

In short, the advantage of plug flow treatment ends after 45 min residence time. Additional bio-oxidation, if required, may best be accomplished in a complete mix basin. Lastly, it is appropriate here to re-emphasize that within an experiment, multiple runs replicate very well, as long as care is taken to biooxidize the COD added in each run.

The regression equation developed for the full body of data is shown in Fig. 9, along with a plot of the equation at three $(\text{COD}/M)_0$'s—0.02, 0.04, and 0.06. These are shown as solid lines. The regression equation was found to have a correlation coefficient of 0.89. An F test indicated that the equation fits the data adequately at the 95% confidence level.

Against the background, shown as dotted lines, are linear regressions for typical individual experiments conducted at close to the 0.02 and 0.06 extremes shown. This comparison demonstrates two key points. First, the maintenance constants obtained in individual runs, ranging from 0.006–0.010 mg/mg hr, were not strikingly different. Therefore, the predicted maintenance constant is a fair representation of the data over the range studied. With regard to the initial rates, on the other hand, we find that at low $(\text{COD}/M)_0$ range the predicted rates are generally lower than that obtained in the individual experiments, and at high $(\text{COD}/M)_0$ the predicted values are somewhat high. Our best explanation for this is that at high $(\text{COD}/M)_0$ there is a shift from a region where first order kinetics is an accurate description of reaction rate to a region where a lower order rate (such as that predicted by Monod kinetics) is more representative of rate phenomenon. Assuming that is the case, the discrepancy at the low end of the $(\text{COD}/M)_0$ range is simply a casualty of the least squares method coping with high range data that does not quite fit the first order model. Thus, while the present correlation fits the data fairly well, a Monod kinetic model offers a possibility of improvement.

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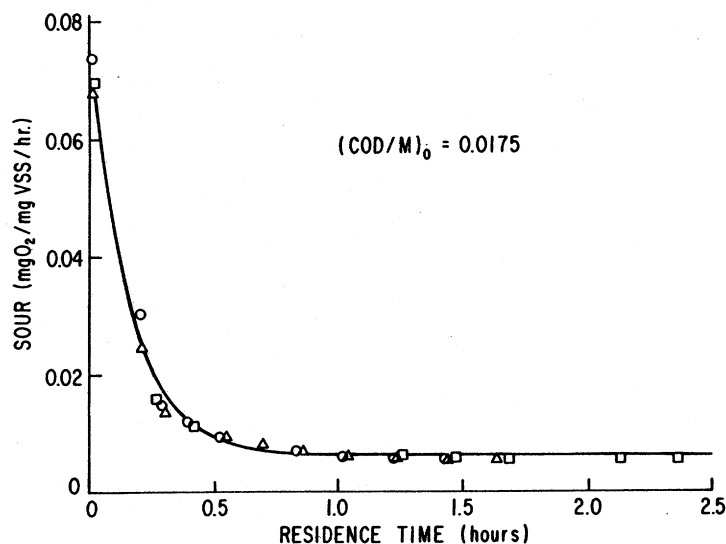


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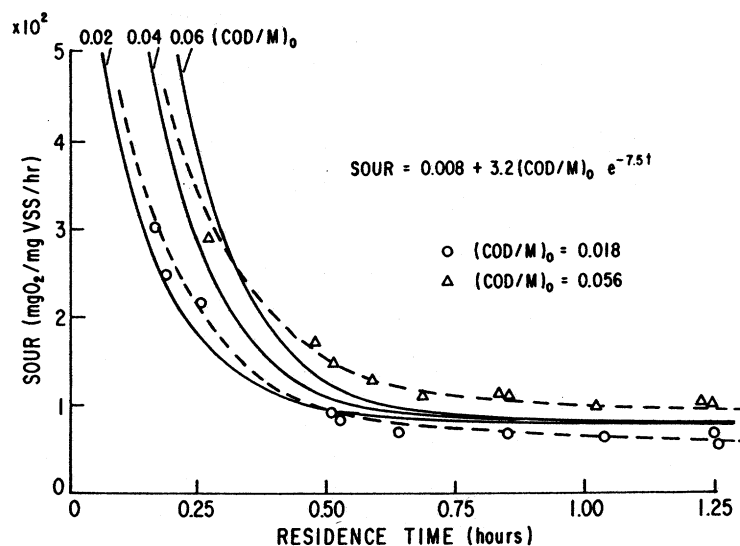


FIG. 9.—Specific Oxygen Uptake Rate Data, Experimental and Predicted Results—Regression Curve for Individual Experiments (Dash)—Regression for Combined Data (Solid Line)

The final element required to transform these relationships to cumulative nitrate relationships, is a yield factor—mg nitrate per mg oxygen. Once obtained, an integrated form of the oxygen relationship shown in Fig. 9 can be converted to the desired nitrate equation. It is generally recognized that the rate of nitrate use per unit mass of sludge is about half the amount one would predict on an electron equivalent basis. Although the discrepancy has not been thoroughly explained, the most satisfying reasons are that in some microbial species, nitrate reductase production is repressed by oxygen present during the aerobic portion of the cycle, while still other species are simply incapable of nitrate reduction. Our results (9) indicate that across the $(\text{COD}/\text{M})_0$ range of interest, the yield factor varies from 40%–50% of the electron equivalent prediction. An average yield factor of 0.45 was used for the following curves. That is, only 0.16 g nitrate nitrogen are utilized per g of oxygen rather than the predicted 0.35 g. In Fig. 10, we show a set of predicted cumulative nitrate removal curves at varying $(\text{COD}/\text{M})_0$ ratios contrasted with experimental data nitrate removal experiments conducted as indicated. Given the sequence of mathematical transformation we have gone through, it is not possible to come up with hard statistics to assess the fit. However, according to an F test, the mean square error in comparing the predicted and experimental nitrate values, is not significantly greater (at $\alpha = 0.05$) than the same mean square error for the original oxygen data. Maintenance and integrated (overall) rates compare favorably with data provided by the EPA (11). Two points are worth stressing here. First, the results confirm the model directly linking oxygen utilization rate and nitrate utilization rate, and in terms of high rates of use of either

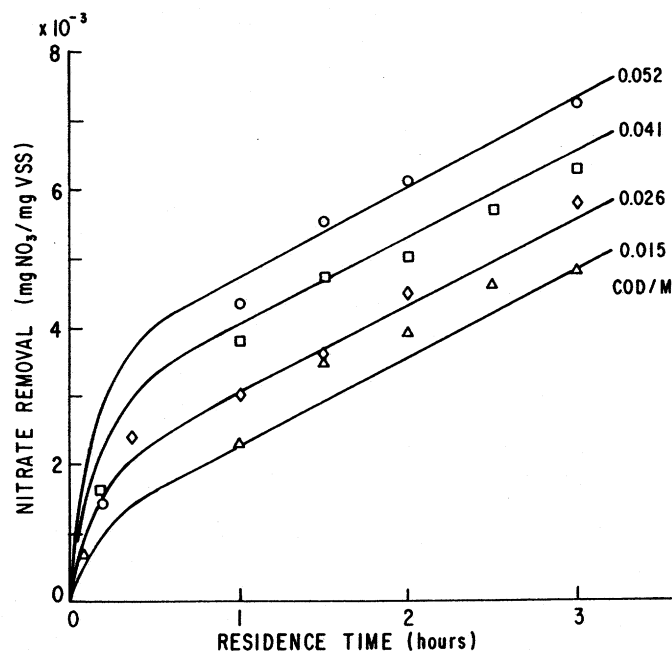


FIG. 10.—Cumulative Nitrate Removal, Predicted from Oxygen Uptake Results

oxidant with accelerated COD consumption. Second, these results suggest that the oxygen utilization approach, should lead to a rational, easy-to-apply method for predicting nitrate utilization that is not significantly less accurate than direct measurement.

CONCLUSIONS

Although there is still room for improvement, oxygen utilization information can be used to predict rates of nitrate utilization. Our results obtained with both nitrate and oxygen confirm the model linking oxidant utilization and COD utilization: in particular the accelerated utilization rates obtainable either at the start of the experiment in a batch system, or at the front end of the treatment basin in a plug flow system. In terms of a continuous system, these accelerated rates are limited to the first 45 min of hydraulic residence time. Lastly, when fully developed, this approach should provide a practical means of designing systems for nitrate reduction utilizing oxygen uptake information either available experimentally or in the literature.

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